

# Application of Essential Oils as green corrosion inhibitors for metals and alloys in different aggressive mediums - A review-

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The use of inhibitors for the protection metals and alloys against corrosion in different aggressive environment is one of the best choices. In recent years, essential oils have been explored as green corrosion inhibitors because to their biodegradability, eco-friendliness, low cost and easy availability. The inhibition performance of these natural products may be to the adsorption, by a synergistic effect, of their different phytochemical constituents including oxygenated monoterpenes and sesquiterpenes as well as hydrocarbons products. The inhibition effectiveness of these green corrosion inhibitors was evaluated by using numerous techniques like weight loss method, polarization study and AC impedance spectra. The protective layer (film) formed on the metal surface has been analyzed by IR spectroscopy, scanning electron microscopy coupled with EDX and X-ray photoelectron spectroscopy (XPS) techniques. This review presents most of the research work published in recent years on the use of essential oils as green corrosion inhibitors for various metals and alloys in different mediums.

**Keywords :** Corrosion inhibitor; Essential oils; Metal ; Alloy; Green inhibitor

## 1. Introduction

Metals and alloys are the most widely used groups of materials, particularly in both mechanical engineering and the transportation industry [1]. In addition, they are commonly used in aggressive environments, such as acids, sea water and caustic solutions in the industry. Therefore, their usefulness is constrained by one common problem known as corrosion. This phenomenon can be defined as the deterioration of a material's properties due to its interaction (chemical or electrochemical) with its environment. It is a complex natural phenomenon that remains a major problem in the world economy and in human security.

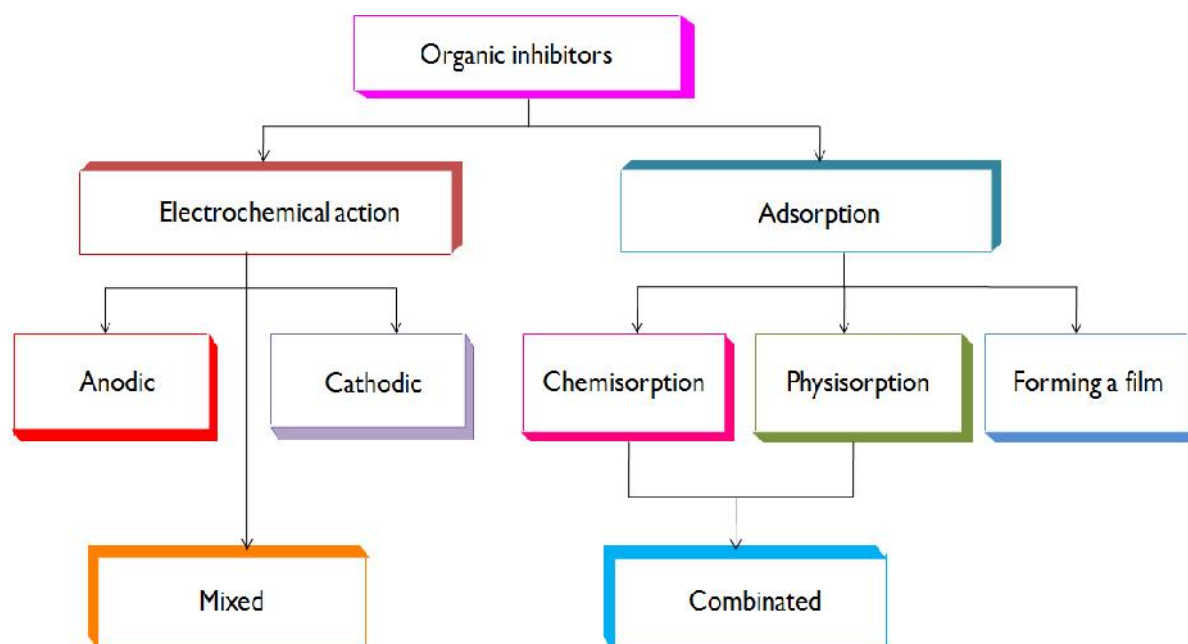
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From an economic viewpoint, corrosion is a source of waste of raw materials and a very high financial source of costs and energy. In addition, it is very costly and has a major impact on the economies of industrial nations causing the direct and indirect loss [2]. So, it is reported that the cost of corrosion of industrialized countries is about 2.5 trillion US dollars, which constitutes approximately 3-4 % of the Gross National Product [3]. Corrosion not only has economic implications, but also poses risks to human life and safety. It presents a public danger by causing serious accidents and hence contributes significantly to environmental pollution [2]. Due to these harmful effects, corrosion is an undesirable phenomenon that ought to be prevented. Thus, several methods available can be employed to slow or prevent corrosion of metallic structures [4]. However, the use of corrosion inhibitor is usually the most economical ways, cost attractive method and the acceptable practices reduce the corrosion rate and protect metal surfaces against corrosion [5].

## 2. Corrosion Inhibitors (Organic and inorganic inhibitors)

Corrosion inhibitor is defined as the solid or liquid substance (or mixtures of substances), which when added in small concentration to an aggressive environment, effectively decrease the corrosion rate and prevent the reaction of the metal with the media [6]. The corrosion inhibitors have been classified into different classes on the bases of their chemical nature, corrosive medium and mechanism of action [7,8]. Indeed, depending on the chemical nature, corrosion inhibitors can be divided into two broad categories, namely inorganic inhibitors, which can be anions or cations, and organic inhibitors that are less toxic than inorganic inhibitors and are now the most used. In addition, according to the mechanism of their action, corrosion inhibitors are classified as anodic inhibitors, cathodic inhibitors or mixed type inhibitors. Anodic inhibitors are substances used to reduce the oxidation corrosion reaction by acting on the anodic sites, due to the forming a protective oxide film on the metal surface and displace the corrosion potential in the positive direction. Cathodic inhibitors reduce the reduction corrosion reaction by acting on the cathodic sites and displace the corrosion potential in the negative direction. So, they inhibit the hydrogen evolution in acidic solutions or the reduction of oxygen in neutral or alkaline solutions. However, mixed-type inhibitors work by reducing both the cathodic and anodic reactions at the same time by decreasing both their electrochemical rates. Otherwise, corrosion inhibitors can be acted by selectively adsorbing on the metal surface and creating a barrier that prevents access of corrosive agents to the metal surface [9].

In general, organic compounds are used as inhibitors in acidic solutions and occasionally, they act as cathodic, anodic or together, mixed inhibitors, nevertheless, they can be interacted chemically or/and electrostatically by mean of adsorption of ions and molecules on the metal surface forming a protective layer. According to the type of interaction, adsorption can be physisorption or chemisorptions or a combination of both [10,11]. Physisorption involves weak bonds that result from electrostatic interactions between ionic charges or dipoles of the adsorbed species and the electric charge of the metal/solution interface; whereas, Chemisorption involves the charge transfer or sharing between the polar part of inhibitor molecules and the metal surface to form a coordinate type bond. The adsorption of organic inhibitors also involves the displacement of water molecules and the formation of a compact barrier film blocking active sites on the metal surface (Fig. 1) [12].



**Fig. 1.** Action mechanism if organic inhibitors.

The adsorption process of corrosion inhibitor depends on various parameters such as temperature, concentration, the nature of the metal's surface, electronic and structural properties of corrosion inhibitor. In order to obtain additional information about the adsorption of inhibitor on metal surface, the degree of surface coverage of the inhibitor must be evaluated as a function of corrosion inhibitor concentration with several adsorption isotherms. Indeed, the Langmuir isotherm assumes that the adsorption takes place at specific homogeneous sites on the surface of the adsorbent forming a monomolecular adsorbed layer and there is no significant interaction among adsorbed species [13]. The Freundlich isotherm

provides an empirical isotherm, which assumes that nonideal adsorption (multilayer sorption) takes place on a heterogeneous surface with different adsorption energy and characters [14]. Temkin adsorption isotherm assumes that the adsorption heat of all adsorbate molecules in adsorbed layer decreases linearly with an increase in the surface coverage. This model contains a factor that obviously considers the adsorbent–adsorbate interactions [15]. The Frumkin isotherm takes into account long-range interactions between adsorbed molecules that can be attractive or repulsive. The logarithmic Temkin isotherm can be considered a special case of the Frumkin isotherm [15]. On the other hand, Langmuir adsorption isotherm is attributing to physisorption or chemisorption phenomenon while Temkin adsorption isotherm gives an explanation about the heterogeneity formed on the metal surface. Chemisorption is attributed to Temkin and Frumkin isotherms [16]. By using the adsorption isotherms various thermodynamic parameters such as changes in free Energy of adsorption ( $G^{\circ}_{\text{ads}}$ ), the entropy of adsorption ( $S^{\circ}_{\text{ads}}$ ), enthalpy of adsorption ( $H^{\circ}_{\text{ads}}$ ) have been calculated. These parameters are useful for clarifying the adsorption behaviour of an inhibitor.

The equilibrium adsorption constant,  $K$  is related to the standard Gibb's free energy of adsorption ( $G^{\circ}_{\text{ads}}$ ) with the following equation:

$$K = \frac{1}{55.5} \cdot \exp \left( - \frac{G^{\circ}_{\text{ads}}}{RT} \right) \quad (1)$$

The standard adsorption enthalpy ( $H^{\circ}_{\text{ads}}$ ) could be calculated on the basis of Van't Hoff equation:

$$\ln K = - \frac{H^{\circ}_{\text{ads}}}{RT} + D \quad (2)$$

where  $R$  is the universal gas constant,  $T$  is the thermodynamic temperature,  $D$  is integration constant, and the value of 55.5 is the concentration of water in the solution in mol/L ( $10^3$  g/L).

Moreover, the standard adsorption entropy ( $S^{\circ}_{\text{ads}}$ ) can be calculated using the following thermodynamic basic Equ. (3).

$$S^{\circ}_{\text{ads}} = \frac{H^{\circ}_{\text{ads}} - G^{\circ}_{\text{ads}}}{T} \quad (3)$$

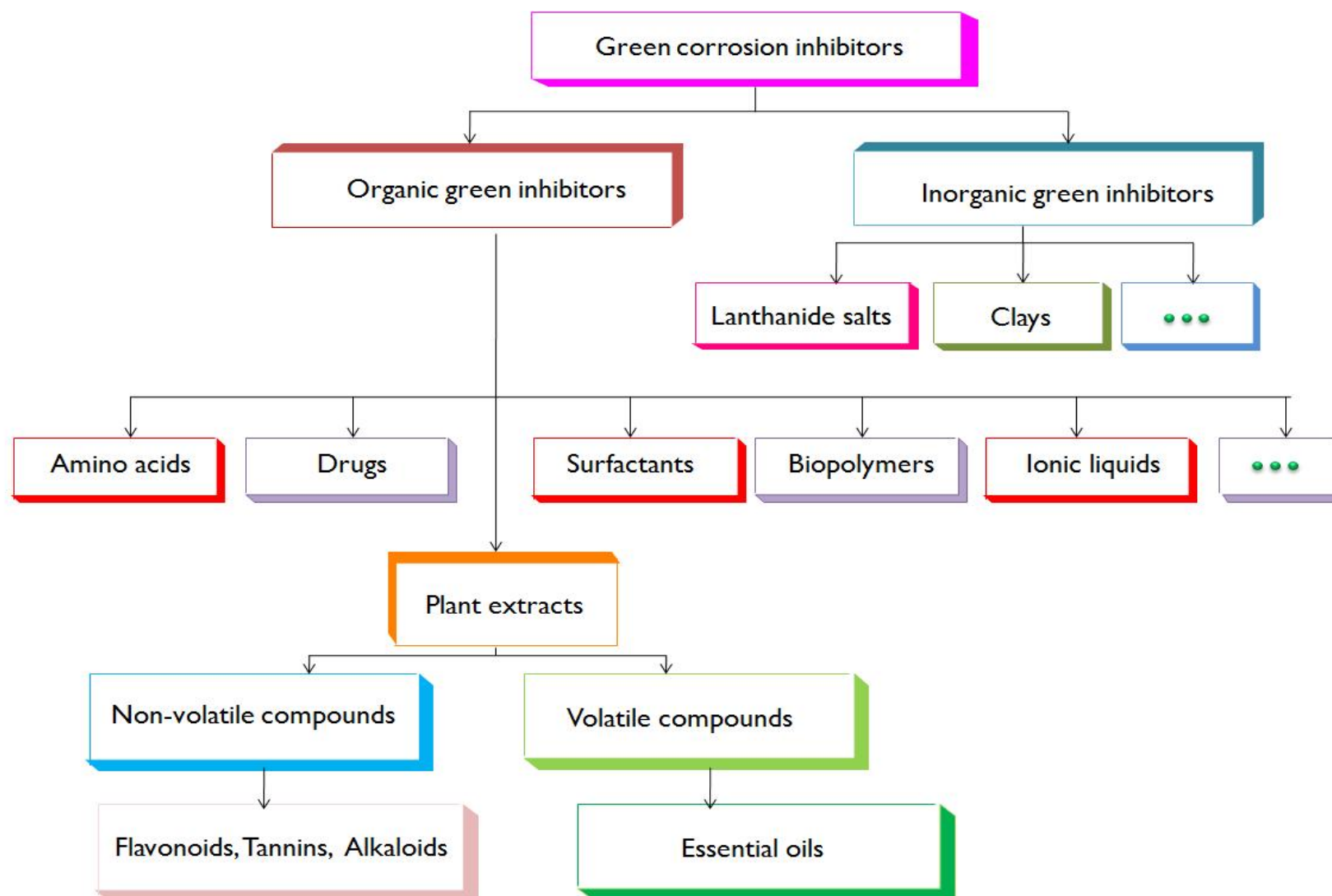
The endothermic process of dissolution ( $H^{\circ}_{\text{ads}} > 0$ ) is attributed to chemisorption, whereas exothermic process ( $H^{\circ}_{\text{ads}} < 0$ ) corresponds to either physisorption or chemisorption, which are distinguished by the absolute value of  $H^{\circ}_{\text{ads}}$ . So, for physisorption process, the absolute

value of  $H^\circ_{\text{ads}}$  is lower than  $40 \text{ KJ.mol}^{-1}$ , while it is approaching to  $100 \text{ KJ.mol}^{-1}$  for chemisorption process [17]. Moreover,  $S^\circ_{\text{ads}}$  sign plays an important role in reflecting whether the order of the inhibitor at the metal/solution interface and indicates whether the adsorption reaction is an associative or dissociative mechanism [18]. According to literature, if the values of  $G^\circ_{\text{ads}}$  is around  $-20 \text{ KJ.mol}^{-1}$  or lower, this indicates that the adsorption process is physical (physisorption) while for value of  $G^\circ_{\text{ads}}$  is around  $-40 \text{ KJ.mol}^{-1}$  or higher, the adsorption process is chemical in nature (chemisorption) [19]. Otherwise, the calculated  $G^\circ_{\text{ads}}$  values ranging between  $-20$  and  $-40 \text{ KJ.mol}^{-1}$ , indicate that the adsorption mechanism of inhibitor may be a combination of both physisorption and chemisorption [19]. In addition, kinetics activation parameters such as activation energy ( $E_a$ ) give also an idea about the type of sorption. Indeed, low values of  $E_a^\circ$  ( $5\text{--}40 \text{ KJ.mol}^{-1}$ ) are characteristics for physisorption, while higher values of  $E_a^\circ$  ( $40\text{--}800 \text{ KJ.mol}^{-1}$ ) suggest chemisorption [20]. The effectiveness of the organic corrosion inhibitors is related to the presence of heterocyclic rings containing polar functional groups, the non-binding doublets of the heteroatoms (N, O, S,...) and conjugated  $\pi$ -electrons of multiple bonds in the molecule. These polar functional groups and conjugated  $\pi$ -electrons possess the high electron density and act as adsorption centers during metal-inhibitor interactions blocking the active corrosion sites and hence reduce the corrosion rate [21,22]. However, most of these substances are not only expensive, but also are highly toxic to cause severe hazards to both human beings and the environment during its application [23]. Hence, these deficiencies have led to the research of green alternative that are environmentally friendly and harmless.

### 3. Green corrosion Inhibitors

Currently, research in corrosion is oriented to the development of “green corrosion inhibitors” (also called “eco-friendly inhibitor”), compounds with good inhibition efficiency (IE), nontoxic and low risk of environmental pollution [24,25]. The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that are readily available, renewable source, do not contain heavy metals or other poisonous compounds and have biodegradability and biocompatibility with the natural environment. They are attracting great interest in the field of “green chemistry” or “eco-friendly” technologies. Similar to the general classification of “conventional corrosion inhibitors”, green inhibitors can be grouped, according to their chemical nature, into two broad categories, namely organic green inhibitors and inorganic green inhibitors [26–28]. It is noticed that organic compounds show higher IE as compared to inorganic and several products are reviewed as organic green corrosion inhibitors for different

metals and various media such as amino acids [26,29,30], polymers and biopolymers [31-34], chemical medicines (drugs) [35-37], surfactants [38,39], ionic liquids (designer chemicals) [40,41] and plant extracts [42-47] (Fig. 2).



**Fig. 2.** Illustration of reported eco-friendly corrosion inhibitors.

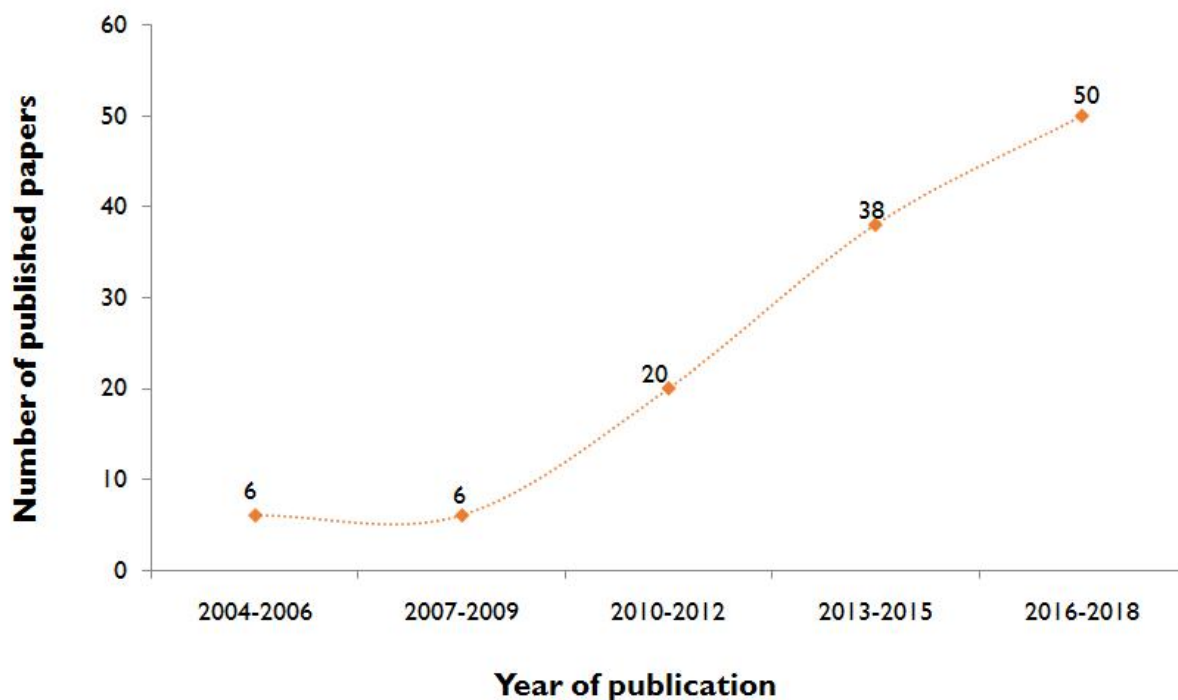
The IE on corrosion of these natural products is attributed to their adsorption by means of heteroatoms localized on functional groups or aromatic rings in their molecular structures. Additionally, these compounds can be interacted via electrostatic or chemical bonds with metal surface to form adsorbed molecular layer, which prevents or limits the contact of the surface with the aggressive agents in solution. In order to investigate the IE of these green inhibitors in various mediums, there are different methods have been employed, including especially Weight loss (WL) method, potentiodynamic polarization (PDP) technique and electrochemical impedance spectroscopy (EIS). Moreover, the protective films formed on metal surfaces have been analyzed by various surface analysis techniques such as Fourier transform infrared spectroscopy (FTIR), Ultraviolet–visible (UV) spectroscopy, X-ray, Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-rays (EDX) and X-ray photoelectron spectroscopy (XPS) techniques etc.

Despite of these promising findings about possible green corrosion inhibitors, most of these substances are limited due to their multi-steps synthesis and extremely expensive [48]. In the same way, the use of organic solvents for the synthesis of certain substances may damage the environment and living beings. Accordingly, it is financially more advantageous to employing an effective mixture which extraction process is simple rather than a substance which its isolation and purification is tedious, laborious, and expensive as well as time-consuming. For these reasons, the use of plant extracts has become an excellent alternative and has a promising future in the field of green chemistry. These extracts have attracted great attention because they are environmentally acceptable, low cost, readily available and biodegradability, in addition to their ecological compatibility [49]. These extracts can be obtained in a simple way and purification methods are not required. In this context, the plant extracts present generally as a complex natural mixture with different molecular structures having different chemical, biological, and physical properties. As shown in Fig. 2 and depending up to their chemical nature, the plant extracts can be schematically divided into two groups containing volatiles and non-volatiles mixture. In the non-volatile group, we will distinguish the flavonoids, the tannins, the polyphenols and the alkaloids while in the group of volatile, we find especially essential oils (EOs). A literature study showed that there are several reviews describing the use of plant extracts as corrosion inhibitors for metals and alloys in a diverse range of corrosive media. However, no detailed review has focused on the application of the EOs as corrosion inhibitors. Therefore, the aim of this review is to present and discuss the sum of published results on this topic.



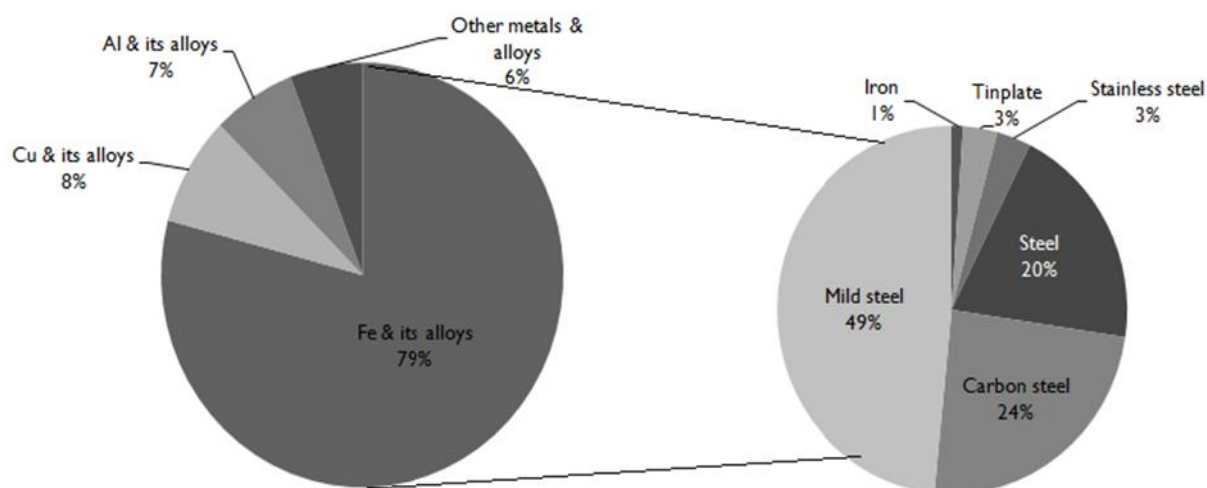
#### 4. Essential oils as green corrosion inhibitors

The term “EO”, used for the first time by Paracelsus von Hohenheim of Switzerland in the sixteenth century, was derived from the drug “*quinta essentia*” [50]. According to the French Agency for Normalization (AFNOR), the term “EO” is reserved for a “product obtained from vegetable raw material, either by distillation with water or steam, or from the epicarp of citrus fruits by a mechanical process, or by dry distillation” [51]. They can be obtained from various parts of the aromatic plants and are stored in specialized storage structures [52]. Although a number of methods are applied to the extraction of EOs, steam distillation or hydrodistillation has become the standard method of EO extraction from plant material [53]. It is simple construction, low cost free solvent and easy to implement. Chemically, EOs are very complex natural mixtures which can contain of up to more than 100 components at quite different concentrations which two or three major components can be present at fairly high concentrations compared to other components present in trace amounts. These components are included in two distinct chemical groups: terpenes and phenylpropanoids. These two groups originate from different precursors of the primary metabolism and are synthesized through separate metabolic pathways [54,55]. The analysis of EOs is generally based on the separation and identification of their constituents by chromatographic techniques and/or spectroscopic methods. Usually, gas chromatography (GC) or coupled with another spectral technique, often mass spectrometry (GC-MS), are most commonly used for routine analyzes of EOs [56]. EOs have generally found their application in various sectors [57,58]. They are used in perfumes, in cosmetics, in pharmacy and aromatherapy, in agriculture and in the food industry, as natural preservatives and additives. As our literature research showed, the first works concerning the evaluation of EOs to act as corrosion inhibitors in aqueous solution were taken in 2004. Lately, the number of articles published for application of these products against corrosion of many metals in a variety of aggressive media increases, in an exponential trend, during 2004-2019 (Fig. 3).



**Fig. 3.** Number of published papers around the subject of EOs as corrosion inhibitors versus year of publication during the last 14 years (until 29 January 2019).

The increasing trend of the number of published papers clearly indicates the importance of exploring the EOs as green corrosion inhibitors. In total, there are 120 published papers that describe anticorrosive activities of 72 samples of EOs extracted from 76 plant species of various origins belonging to 18 distinct families. As can be seen in Fig. 4, many of these publications are focused on finding corrosion inhibitors for iron and its alloys representing 79% of the total papers, followed by copper and its alloys (8%), aluminum and its alloys (7%) and other metals and alloys with 6%.



**Fig. 4.** The distribution of published papers on EOs as corrosion inhibitors for various metals in various aqueous media.

In addition, Fig. 4 show that 95 research papers, accounting for 79% of the total, are focused on the use of EOs as corrosion inhibitors against iron and its alloys. Most of these papers (91 publications), representing 95%, are devoted to evaluating this property for steel and its alloys including 46 publications for mild steel (48%), 23 for carbon steel (24%) and 19 for steel (20%) and 3 for stainless steel (3%). This particular importance can be explained by the wide use of steel in a broad spectrum of industries and machinery; however, its tendency to corrosion made it inadequate for exposures in contact with aggressive acids [59]. Indeed, it is estimated that corrosion destroys one quarter of the world's annual steel production, which corresponds to about 150 million tons per year, or 5 tons per second [60]. This can be related to the tremendous applications of those metallic materials in different industry fields, which implied more the interest of researchers. As well, the other metals and their alloys are the most important metals and are used in a large number of applications because of some favorable properties such as excellent thermal conductivity, mechanical workability, and physical properties and malleability [61,62]. They show also a considerable resistance against different types of corrosion due to the formation of a protective layer on their surfaces [63,64]. However, they are susceptible to corrosion when they are exposed to aggressive environments. Thus, to stop or delay to the maximum attack of the metals, the use of corrosion inhibitors in such conditions is necessary. Accordingly, this review describes the extant research on several EOs obtained exclusively by hydrodistillation or steam distillation as green corrosion inhibitors against corrosion of various metals in different aqueous corrosive environments. Table 1 summarize their relative natural source of EOs, the protected metal and the corrosive environment, the IE, the specific adsorption mechanisms and adsorption isotherm models. Each inhibitor's percentage of IE is reported at the maximum value according to conditions of study in each reference.

**Table 1.** Essential oils used as green corrosion inhibitors for metals and alloys in various media.

EO inhibitor	Medium	Inhibitor type	Type of metal	Maximum IE (%)	Adsorption mechanism	Adsorption isotherm	Ref.
<i>Artemisia herba alba</i>	1M HCl	Cathodic inhibitor	Steel	76 % at 19 g/dm <sup>3</sup>	Chemisorption	Frumkin	[65]
<i>Artemisia herba alba</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Cathodic inhibitor	Steel	74 % at 1 g/L	Chimisorption	-	[66]
<i>Artemisia herba alba</i>	2M H <sub>3</sub> PO <sub>4</sub>	Cathodic inhibitor	Steel	79 % at 6 g/L	Physisorption	Langmuir	[67]
<i>Artemisia herba alba</i>	0.5M HCl	Mixed inhibitor	Tinplate	95 % at 6 g/L	Physisorption	Langmuir	[68]
<i>Artemisia herba alba</i>	1M HCl 1M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Stainless steels: 2205 DSS 2507 DSS	1M HCl at 10 g/L 2205 DSS : 79 % 2507 DSS : 93 % 1M H <sub>2</sub> SO <sub>4</sub> at 5 g/L 2205 DSS: 3 % 2507 DSS: 38 %	-	-	[69]
<i>Artemisia herba alba</i>	20% H <sub>2</sub> SO <sub>4</sub>	Cathodic inhibitor	X52 steel	98.29 % at 1200 ppm	-	Langmuir	[70]
<i>Artemisia herba alba</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	88 % at 2.76 g/L	Physisorption	Langmuir	[71]
<i>Artemisia mesatlantica</i>	1M HCl	-	Mild steel	91 % at 2.76 g/L	Physisorption	Langmuir and El-Awady	[72]
<i>Artemisia mesatlantica</i>	1M HCl	Mixed inhibitor	Carbon steel	92 % at 3 g/L	Physisorption	Langmuir	[73]
<i>Artemisia abrotanum</i>	1M HCl	Mixed inhibitor	Mild steel	83.9 % at 2 g/L	-	Langmuir	[74]
<i>Rosmarinus officinalis</i>	3M HCl	Cathodic inhibitor	Steel	-	Physisorption	Frumkin	[75]
<i>Rosmarinus officinalis</i>	2M H <sub>3</sub> PO <sub>4</sub>	Cathodic inhibitor	Steel	73 % at 10 g/L	Physisorption	Frumkin	[76]
<i>Rosmarinus officinalis</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Cathodic inhibitor	C38 steel	61 % at 1 g/L	-	-	[77]
<i>Rosmarinus officinalis</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Cathodic inhibitor	Carbon steel	94.28 % at 600 ppm	Physisorption	Langmuir	[78]
<i>Rosmarinus officinalis</i>	1M HCl 1M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Stainless steels: 2205 DSS 2507 DSS	2205 at 10 g/L 1M HCl: 19 % 1M H <sub>2</sub> SO <sub>4</sub> : 36 % 2507 at 5 g/L 1M HCl: 57 % 1M H <sub>2</sub> SO <sub>4</sub> : 4 %	-	-	[69]

<i>Eucalyptus globulus</i>	1M HCl	Cathodic inhibitor	Steel	72% at 3 mL/L	-	Frumkin	[79]
<i>Eucalyptus globulus</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	C38 Steel	81 % at 6 g/L	Physisorption	Langmuir	[80]
<i>Eucalyptus globulus</i>	0.5M HCl	Mixed inhibitor	Mild steel	92 % at 5 g/L	Physisorption	-	[81]
<i>Eucalyptus globulus</i>	1M HCl 1M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Stainless steels: 2205 DSS 2507 DSS	1M HCl 2205: 70% at 2.5 g/L 2507 : 64 % 10 g/L 1M H <sub>2</sub> SO <sub>4</sub> 2205 : 13% 5g/L 2507 : 67 % 10 g/L	-	-	[69]
<i>Foeniculum vulgare (seeds)</i>	1M HCl	Mixed inhibitor	C38 Steel	76 % at 3 mL/L	Physisorption	-	[82]
<i>Foeniculum vulgare (seeds)</i>	1M HCl	Mixed inhibitor	Mild steel	91.5 % at 1 g/L	Physisorption	-	[83]
<i>Foeniculum vulgare (bulbs)</i>	1M HCl	Mixed inhibitor	Mild steel	90,6 % at 1 g/L	Physisorption		[84]
<i>Foeniculum vulgare (leaves)</i>	1M HCl	Mixed inhibitor	Mild steel	92.46 % at 1 g/L	Physisorption		[85]
<i>Foeniculum vulgare (seeds)</i>	1M HCl	Mixed inhibitor	304 stainless steel	77.2 % at 150 ppm	Physisorption	Langmuir	[86]
<i>Syzygium aromaticum (Clove)</i>	1M HCl	Mixed inhibitor	Mild steel	93.4 % at 0.8 g/L	-		[87]
<i>Syzygium aromaticum</i>	2M H <sub>3</sub> PO <sub>4</sub>	Mixed inhibitor	Mild steel	87 % 1 g/L	Physisorption	Langmuir	[88]
<i>Syzygium aromaticum</i>	Acids	-	Mild steel	-	Combinated adsorption	-	[89]
<i>Syzygium aromaticum</i>	0.5M HCl	-	Iron	91.41 % at 6 g/L	Physisorption	Langmuir	[90]
<i>Carum carvi (seeds)</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	86 % at 50 ppm	-	-	[91]
<i>Carum carvi</i>	1M HCl	Mixed inhibitor	Mild steel	88 % at 3 g/L	Physisorption	Langmuir	[92]
<i>Carum carvi (seeds)</i>	1M HCl	Cathodic inhibitor	C38 steel	92 % at 3 g/L	Physisorption	Langmuir	[93]
<i>Carum carvi (seeds)</i>	1M HCl	Mixed inhibitor	Carbon steel	94% at 1g/L	Physisorption	-	[94]
<i>Tetraclinis articulata</i>	1M HCl	Mixed inhibitor	Carbon steel	80% at 2g/L	Physisorption	Langmuir	[95]
<i>Tetraclinis articulata</i>	0.1N HCl	Mixed inhibitor	Carbon steel	74.7 % at 30 µL	Combinated adsorption	-	[96]
<i>Tetraclinis articulata</i>	0.1N H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Carbon steel	63.6 % at 30 µL		-	
<i>Tetraclinis articulata</i>	0.1N HNO <sub>3</sub>	Mixed inhibitor	Carbon steel	70.5 % at 30 µL		-	
<i>Mentha pulegium</i>	1M HCl	Cathodic inhibitor	Steel	80 % at 2.76 g/L	Chemisorption	Frumkin	[97]
<i>Mentha pulegium</i>	1M HCl	Mixed inhibitor	Mild steel	90 % at 1g/L	-	-	[98]

<i>Mentha pulegium</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	89.7 % at 4g/L	Chemisorption	Langmuir	[99]
<i>Mentha piperita</i>	1M HCl	Mixed inhibitor	Mild steel	86 % at 1g/L	-	-	[98]
<i>Mentha piperita</i>	1M HCl	Mixed inhibitor	Mild steel	87 % at 0.7 g/L	Physisorption	Langmuir	[100]
<i>Mentha piperita</i>	2M H <sub>3</sub> PO <sub>4</sub>	-	Mild steel	50.17 % at 1 mL/L	Physisorption	-	[101]
<i>Pistacia lentiscus</i>	1M HCl	Mixed inhibitor	Mild steel	96.34 % at 1g/L	Physisorption	Langmuir	[102]
<i>Pistacia lentiscus</i>	1M HCl	Mixed inhibitor	Mild steel	90.8 % at 2.56 g/L	Physisorption	El-Awady et al	[103]
<i>Pistacia lentiscus</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Carbon steel	87.12 % at 1 g/L	-	Langmuir	[104]
<i>Pistacia lentiscus</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	81.2 % at 2g/L	Physisorption	Langmuir	[105]
<i>Lavandula dentata</i>	1M HCl	Cathodic inhibitor	Steel	90 % at 2 g/L	Chemisorption	Langmuir	[106]
<i>Lavandula dentata</i>	1M HCl	Anodic inhibitor	Mild steel	70 % at 5 mL/L	Physisorption	-	[107]
<i>Lavandula stoechas</i>	1M HCl	Mixed inhibitor	C35E steel	84.35 % at 0.5 g/L	Physisorption	Langmuir	[108]
<i>Lavandula stoechas</i>	1M HCl	Mixed inhibitor	C38 steel	76.19 % at 2 g/L	Physisorption	Langmuir	[109]
<i>Lavandula stoechas</i>	5.5M H <sub>3</sub> PO <sub>4</sub>	Anodic inhibitor	Stainless steel UB6	89 % at 1.2 g/L.	Physisorption	Langmuir	[110]
<i>Lavandula pedunculata</i>	1M HCl	Mixed inhibitor	Mild steel	88 % at 3 g/L	-	Langmuir	[111]
<i>Lavandula multifida</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	C38 steel	72.2 % at 2 g/L	Chemisorption	Langmuir	[112]
<i>Cedrus atlantica</i>	1M HC	Cathodic inhibitor	Steel	72 % at 9 mL/L	Chimisorption	Temkin	[113]
<i>Cedrus atlantica</i>	1M HCl	Mixed inhibitor	Steel S300	88 % at 1 g/L	Chimisorption	Langmuir	[114]
<i>Juniperus Phoenicea</i>	1M HCl	Mixed inhibitor	Mild steel	88.3 % at 250 ppm	-	-	[115]
<i>Juniperus Phoenicea</i>	1M HCl	Mixed inhibitor	Mild steel	83 % at 1500 ppm	Physisorption	-	[116]
<i>Orange peel</i>	1N HCl	Mixed inhibitor	Mild steel	94.8 % at 3 g/L	-	-	[117]
<i>Orange peel</i>	1N H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	92.5 % at 3 g/L	-	-	
<i>Jasminum grandiflorum</i>	0.005M HCl and 0.01M HCl	Mixed inhibitor	Mild steel	93.3 % (0.005M) and 88.2 % (0.01M) HCl at 4% (v/v)	-	-	[118]
<i>Jasminum grandiflorum</i>	0.005 NaCl 0.01 NaCl 0.05 NaCl 0.1M NaCl	Mixed inhibitor	Mild steel	90.2 % (0.005M), 89.6 % (0.01M) 81.7 % (0.1M) NaCl at 4% (v/v)	Chemisorption	Temkin	[119]



<i>Mentha rotundifolia</i>	1M HCl	Mixed inhibitor	Carbon steel	87 % at 2 mL/L	Combined adsorption	Langmuir	[120]
<i>Mentha rotundifolia</i>	1M HCl	Cathodic inhibitor	Mild steel	78.88 % at 2 g/L	Physiosorption	Langmuir	[121]
<i>Mentha spicata</i>	1M HCl	Mixed inhibitor	Steel	97 % at 2 g/L	Physiosorption	Langmuir	[122]
<i>Mentha suaveolens</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	81 % at 1 g/L	-	Langmuir	[123]
<i>Thymus satureioides</i>	0. M HCl	Mixed inhibitor	Tinplate	87 % at 6 g/L	Physiosorption	-	[124]
<i>Thymus satureioides mixed</i> <i>Cosmetic Argania spinosa</i> (98% CAO+2% TS)	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Carbon steel	96 % at 4 g/L	-	-	[125]
<i>Thymus pallidus</i>	1M HCl	Mixed inhibitor	Carbon Steel	88.65 % at 1 g/L	Physiosorption	Langmuir	[126]
<i>Thymus algeriensis</i>	1M HCl	Mixed inhibitor	Mild steel	81 % at 1g/L	-	Langmuir	[127]
<i>Thymus vulgaris</i>	1M HCl	Mixed inhibitor	Mild steel	95,7 % at 2 g/L	Chemisorption	Langmuir	[128]
<i>Thymus capitatus</i>	1M HCl	Mixed inhibitor	Mild steel	68 % at 5 mL/L	-	-	[129]
<i>Thymus leptobotrys</i>	1M HCl	Mixed inhibitor	Carbon steel	86.95 % at 2 g/L.	-	Langmuir	[130]
<i>Thymus sahraouian</i>	1M HCl	Mixed inhibitor	Mild steel	77.82 % at 2 g/L	Physiosorption	Langmuir	[131]
<i>Thymus munbyanus</i>	1M HCl	Mixed inhibitor	Mild steel	80.66 % at 3 g/L	-	Langmuir	[132]
<i>Pulicaria mauritanica</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	91.5 % at 2 g/L	Chemisorption	Langmuir	[133]
<i>Pulicaria mauritanica</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	95.08 % at 2g/L	Physiosorption	Langmuir	[134]
<i>Salvia officinalis</i>	1M HCl	Mixed inhibitor	Mild steel	85.05 % at 8 mL/L	Physiosorption	-	[135]
<i>Salvia officinalis</i> + <i>Simmondsia chinensi</i>	1M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	86.58 % at 6% (v/v)	Chemisorption	Langmuir	[136]
<i>Salvia aucheri mesatlantica</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Steel	86.12 % at 2 g/L	Chemisorption	Langmuir	[137]
<i>Jasminum auriculatum</i>	0.005M and 0.01M HCl	Mixed inhibitor	Mild steel	93.1 % (0.005M) and 87.4 % (0.01M) HCl at 4% (v/v)	-	-	[118]
<i>Oleum palmarosae</i>	0.005M and 0.01M HCl	Mixed inhibitor	Mild steel	95.1 % (0.005M) and 89.8 % (0.01M) HCl at 4% (v/v)	-	-	

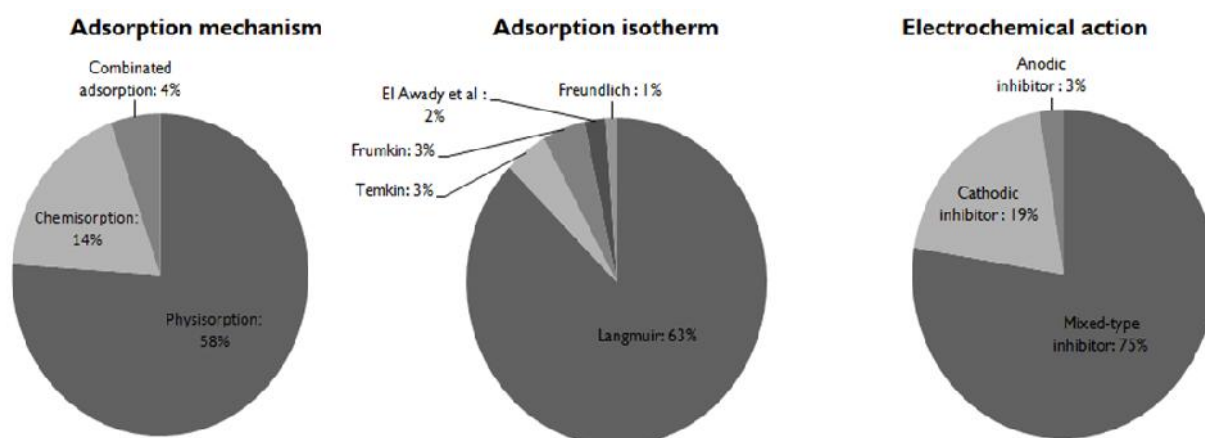
<i>Ocimum basilicum</i>	0.005M and 0.01M HCl	Mixed inhibitor	Mild steel	91.8 % (0.005M) and 86.4 % (0.01M) HCl at 4% (v/v)	-	-	
<i>Etiveria zizanioides</i>	0.005M and 0.01M HCl	Mixed inhibitor	Mild steel	95.5 % (0.005M) and 90.3 % (0.01M) HCl at 4% (v/v)	-	-	
<i>Chamomilla recutita</i>	1M HCl	Mixed inhibitor	Steel	90 % at 2 g/L	-	-	[138]
<i>Lippia alba</i>	0.5M HCl	Mixed inhibitor	Mild steel	92.6 % at 5 g/L	Physisorption	-	[81]
<i>Verbena officinalis</i>	1M HCl	Mixed inhibitor	C38 steel	86.8 % at 5 g/L	Physisorption	Langmuir	[139]
<i>Allium sativum</i> (Garlic)	1M HCl	Mixed inhibitor	Carbon steel	95.8 % at 2.5 g/L	Physisorption	Langmuir	[140]
<i>Ruta chalepensis</i>	1M HCl	Mixed inhibitor	Steel	77 % at 2.5 mL/L	Physisorption	Langmuir	[141]
<i>Linum usitatissimum</i> (Linseed)	1M HCl	Mixed inhibitor	Carbon steel	98.2 % at 3 g/L	Chimisorption	Langmuir	[142]
<i>Pelargonium</i>	1M HCl	Mixed inhibitor	Steel	90.61 % at 4 mL/L	Physisorption	Langmuir	[143]
<i>Ptychotis verticillata</i>	1M HCl	Mixed inhibitor	Mild steel	74.6 % at 1.08 g/L	-	Langmuir	[144]
<i>Melissa officinalis</i>	1M HCl	Mixed inhibitor	Carbon steel	94.7 % at 2g/L	-	Langmuir	[145]
<i>Citrus aurantium</i>	M HCl	Mixed inhibitor	Mild steel	95 % at 5 g/L	-	Langmuir	[146]
<i>Melaleuca quinquenervia</i> (Niaouli)	3% NaCl	Cathodic inhibitor at 0.1-0.4 g/L Mixed inhibitor at 0.5 g/L	Tinplate	88 % at 0.5 g/L	Physisorption	Langmuir	[147]
<i>Alpinia galanga</i>	1M HCl	-	Mild steel	88.5 % at 775 ppm	Physisorption	Langmuir	[148]
<i>Grape fruit</i>	1M HCl	-	Carbon steel	86.15 % at 1g/L	Physisorption	Langmuir	[149]
<i>Grape fruit</i>	2M H <sub>3</sub> PO <sub>4</sub>	-	Mild steel	48.94 % at 1 mL/L	Physisorption	-	[101]
<i>Piper nigrum</i>	1M HCl	Mixed inhibitor	Mild steel	85.65 % at 0.6 g/L (HD) 90.6 % at 0.6 g/L (MHD)	-	Langmuir	[150]
<i>Apium graveolens</i> (Celery)	1M HCl	Mixed inhibitor	C35 steel	96.66 % at 1 g/L	Physisorption	Langmuir	[151]
<i>Warionia saharea</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	-	Mild steel	74 % at 3 g/L	Physisorption	Langmuir	[152]



<i>Asteriscus graveolens</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Mixed inhibitor	Mild steel	82.89 % at 3 g/L	Physisorption	Langmuir	[153]
<i>Helichrysum italicum subsp. italicum</i>	1M HCl	-	Mild steel	82.33 % at 2 g/L	Physisorption	Langmuir	[154]
<i>Senecio inaequidens</i>	1M HCl	-	Mild steel	90.56 % at 2 g/L	Physisorption	Langmuir	[155]
<i>Eryngium maritimum</i>	1M HCl	-	Mild steel	97.91 % at 2 mg/mL	Physisorption	Langmuir	[156]
<i>Ammodaucus leucotrichus</i>	1M HCl	Mixed inhibitor	Mild steel	84.32 % at 3 g/L	Physiosorption	Langmuir	[157]
<i>Limbarda crithmoides</i>	1M HCl	-	Mild steel	77.85 % at 2 g/L	Physiosorption	Langmuir	[158]
<i>Artemisia herba alba</i>	2M H <sub>3</sub> PO <sub>4</sub> + 3.10-1 M NaCl	Mixed inhibitor	Copper	89 % at 6 g/L	Physisorption	-	[159]
<i>Artemisia herba alba</i>	2M HNO <sub>3</sub>	Mixed inhibitor	Copper	91 % at 250 ppm	Physisorption	Langmuir	[160]
<i>Thymus satureoides</i>	2M HNO <sub>3</sub>	Mixed inhibitor	Copper	89.04 % at 1200 ppm	Physisorption	Langmuir	[161]
<i>Eugenia caryophyllus (Clove)</i>	2M HNO <sub>3</sub>	Cathodic inhibitor	Copper	70 % at 1600 ppm	Chemisorption	Langmuir	[162]
<i>Cinnamomum verum (Cinnamon)</i>	3% NaCl	Mixed inhibitor	Copper	85 % at 150 ppm	-	-	[163]
<i>Cinnamomum verum (Cinnamon)</i>	0.5M H <sub>2</sub> SO <sub>4</sub>	Cathodic inhibitor	Copper	89.62 % at 150 ppm	Physisorption	Langmuir	[164]
<i>Myrtus communis</i>	2M HNO <sub>3</sub>	Anodic inhibitor	Copper	73 % at 1800 ppm	Physisorption	-	[165]
<i>Myrtus communis</i>	3% NaCl	Cathodic inhibitor	Brass (Cu70-Zn30)	83 % at 2 g/L	Physisorption	-	[166]
<i>Nigella sativa</i>	1M HCl	Mixed inhibitor	Brass	79 % at 1.5 g/L	-	-	[167]
<i>Elettaria cardamomum</i>	1M HCl	Mixed inhibitor	Brass	72.5 % at 1.5 g/L	-	-	
<i>Citrus limon</i>	1M HNO <sub>3</sub>	Mixed inhibitor	-Brass	93.65 % at 5 mL/L	Physisorption	Temkin	[168]
<i>Anethum graveolens</i>	1M HCl	Cathodic inhibitor	Aluminium	96.9 % at 300 ppm	Physisorption	Langmuir	[169]
<i>Ocimum basilicum</i>	0.5M HCl	Mixed inhibitor	Aluminium	90 % at 5.7 g/L	Physisorption	Langmuir	[170]
<i>Mentha spicata</i>	1M HCl	Mixed inhibitor	Aluminum	83,01 % at 1800 ppm	Physisorption	Langmuir	[171]
<i>Laurus nobilis</i>	3% NaCl	Cathodic inhibitor	Aluminium	91% at 50 ppm	-	Langmuir	[172]
<i>Laurus nobilis</i>	3% NaCl	Cathodic inhibitor	AA5754 aluminium	82.4 % at 50 ppm	-	Langmuir	
<i>Laurus nobilis</i>	1% Acetic acid	Anodic inhibitor	Aluminium	68.9 % at 45 mg/L	Physisorption	Freundlich	[173]

<i>Laurus nobilis</i>	1% Acetic acid	Cathodic inhibitor	AA5754 aluminium	84.4 % at 45 mg/L	Combinated adsorption	Temkin	
<i>Lippia citriodora</i>	1M HCl	Mixed inhibitor	Aluminum	98.35 % at 1200 ppm	Chemisorption	Langmuir	[174]
<i>Mentha pulegium</i>	2M H <sub>3</sub> PO <sub>4</sub>	Cathodic inhibitor	Aluminium	79 % at 1800 ppm	Chemisorption	-	[175]
<i>Lavandula angustifolia</i>	3% NaCl	Cathodic inhibitor	Al-3Mg	99 % at 20 ppm	Combinated adsorption	Langmuir	[176]
<i>Rosmarinus officinalis</i>	0.1M HCl	Mixed inhibitor	Nickel Inconel 600 Inconel 690	93.28 % at 250 ppm 95.53 % at 250 ppm 99.81 % at 250 ppm	-	Langmuir	[177]
<i>Syzygium aromaticum</i> (Clove)	0.1M HCl	Mixed inhibitor	Nickel Inconel 600 Inconel 690	86.09 % at 250 ppm 88.34 % at 250 ppm 92.48 % at 250 ppm	-	Langmuir	[178]
<i>Nigella sativa</i> (black cumin)	0.1M HCl	Mixed inhibitor	Nickel	83.45 % at 250 ppm	Physisorption	Langmuir	[179]
<i>Eucalyptus camaldulensis</i>	0.1M Na <sub>2</sub> CO <sub>3</sub>	Mixed inhibitor	Lead	75.81 % at 1800 ppm	Physisorption	Langmuir	[180]
<i>Artemisia herba alba</i>	0.1M Na <sub>2</sub> CO <sub>3</sub>	Mixed inhibitor	Lead	77 % at 2000 ppm	Physisorption	-	[181]
<i>Cedrus atlantica</i>	0.1M Na <sub>2</sub> CO <sub>3</sub>	Cathodic inhibitor	Lead	70 % at 2000 ppm	Physisorption		[182]
<i>Mentha viridis</i>	0.1M Na <sub>2</sub> CO <sub>3</sub>	Mixed inhibitor	Lead	80 % at 2000 ppm	Physisorption	Langmuir	[183]

This is the first extensive review describing the application of EOs for corrosion inhibition of metals and alloys, based on the research papers from the last 14 years (2004–2018). In total, 120 published papers described the anticorrosive activities of 72 different samples of essential oils extracted from 76 plant species belonging to 18 distinct families. From the above mentioned tables, all EOs acted as better corrosion inhibitors of the corrosion of all metals in a dose dependent manner. The IE increased significantly with increasing concentrations of the tested natural products in the different test media. This indicates that the active molecules of the extracts are adsorbed onto the metal surfaces, through the formation of insoluble intermediates, resulting in the blocking of the active sites and effectively isolating the metals and corrosive agents. Moreover, the IE of the majority of the studied materials increased with increasing temperature in tested range.



**Fig. 5.** Percentage of various type actions of studied EOs used for corrosion inhibition of metals and its alloys studied in the articles covered in this review.

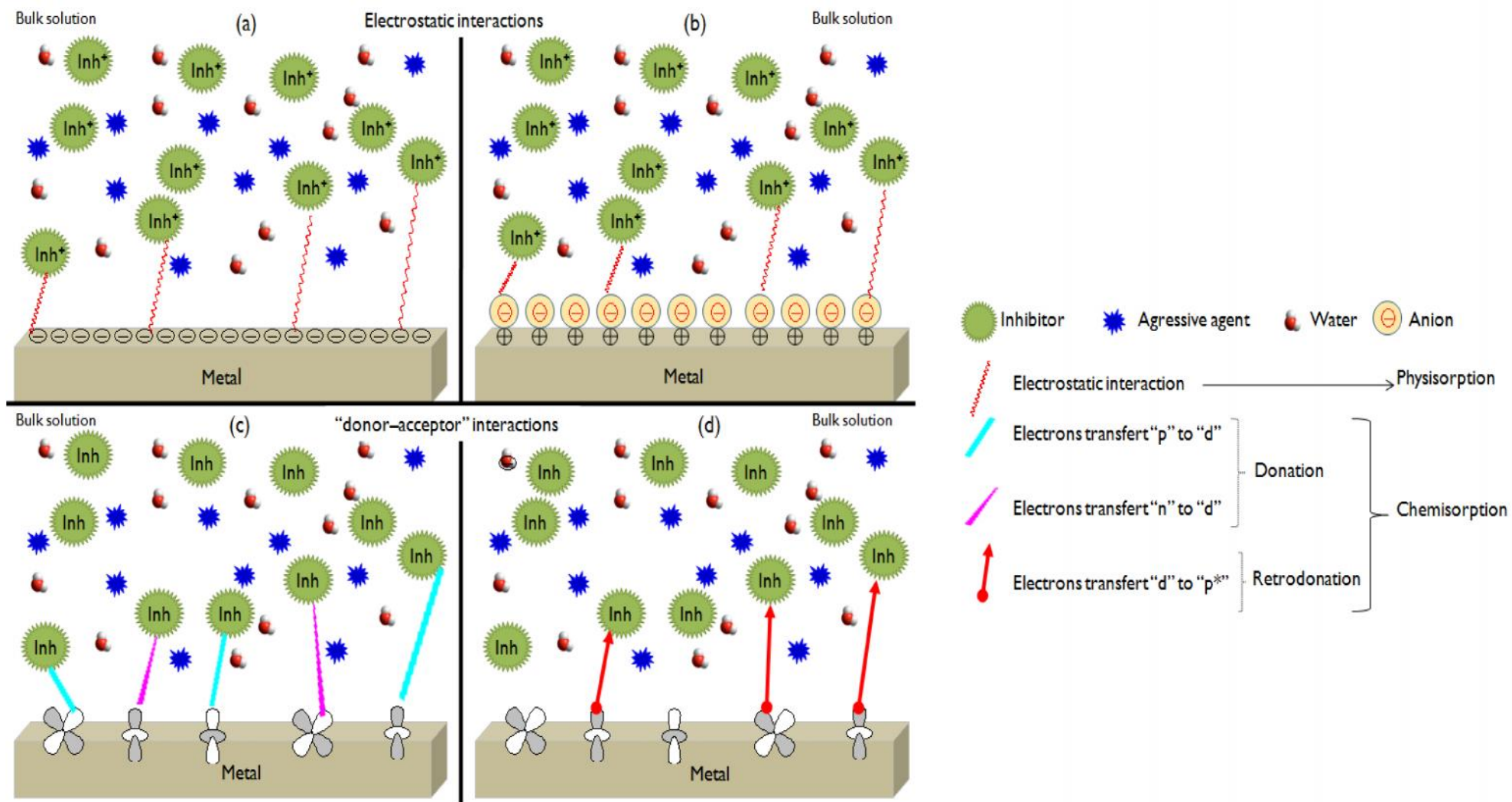
As seen in Fig. 5, most of studied corrosion inhibitors behave as a mixed-type corrosion inhibitor and their inhibition action occurs primarily through physisorption mechanism and follow Langmuir adsorption isotherm. Indeed, according to the thermodynamic calculations, 70 research papers, representing 58% of the total papers, describe that 41 of studied samples are physically adsorbed on the metal surface, 17 research papers, accounting to 14% of the total papers, revealed that 14 of studied samples are chemically adsorbed on the metal surface, whereas only 5 research papers (4% of the total papers) showed that both chemical and physical adsorption modes were proposed as the mechanism for 5 of studied samples. By analysis of adsorption isotherm curves, it is found that the adsorption of 71 of studied materials which present 63% of published work obeyed Langmuir adsorption isotherm, 4 of

studied samples, representing 3% of the total papers, follows Temkin adsorption isotherm, 4 other studied samples which present 3% of published work obeyed Frumkin's adsorption isotherm, 2 of the studied samples (2% of the total papers) follows El Awady et al adsorption and one sample obeyed Freundlich adsorption isotherm. Moreover, the electrochemical measurements indicated that 71 of the studied materials which, representing 90 research papers (75% of the total papers), acts as a mixed-type inhibitor, 16 of the studied samples (23 research papers representing 19% of the total papers) acts as a cathodic inhibitor and only 3 of the studied samples (3 research papers accounting 3% of the total papers) acts as an anodic inhibitor. The reproducibility of results strongly depends upon several factors such sample, nature and surface charge of the metal, type and concentration of aggressive electrolyte. It should also be noted that some studied samples at specific concentrations are strictly metal or alloy and corrosive medium and may have low inhibition with others.

## 5. Mechanism of inhibition

The adsorption of EOs molecules at the metal/solution interface is the first step in inhibition of metallic corrosion, and quantum chemical calculations show that the inhibitor molecules exist in both neutral, which may be adsorbed on the surface through a chemisorption mechanism ("donor–acceptor" interactions), charged forms which can be interacted electrostatically with charged metal surface (physisorption) or as a combination of both. Also, the adsorption process is affected by the chemical structures of the EOs molecules, the nature and charged surface of the metal and the distribution of charge over the whole inhibitor molecules. According to previous results presented in this review, essential oils have shown a good ability to control corrosion of different metallic materials in various environments. Their inhibition performance was closely related to their chemical composition which includes a non-polar, hydrophobic, consisting of hydrocarbon molecules and a polar, hydrophilic, which presents one or more functional group including oxygenated monoterpenes and sesquiterpenes [184]. Owing to this complexity, it is quite difficult to assign the inhibiting effect to a particular constituent, nevertheless, it is possible to the inhibition effectiveness of these extracts might be related to one specific molecule, especially major compound, or those susceptible to be active, or to a synergistic effect of the entire extract. Indeed, the inhibition efficiency of hydrocarbon terpenes could be attributed to the presence of a hydrophobic film in contact with the metal surface, which is constant and that somehow contribute to the interaction between the compounds or corrosive species and metal [185,186]. Moreover, the inhibition efficiency of oxygenated terpenes could be attributed to the presence of Oxygen

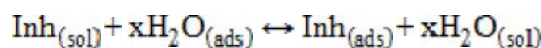
atoms in functional groups (O–H, C=O, C–O,) and  $\pi$ -electrons of the aromatic ring or the double bonds in their structure, which meets the general characteristics of typical corrosion inhibitors. Thus, it is reasonable to deduce that the oxygenated compounds in EOs exhibit the inhibition performance. Indeed, two modes of adsorption are considered on the metal surface in aqueous solution. In the first mode, the charged molecules may be adsorbed on the surface of metal with opposite charge through electrostatic interactions (physisorption mechanism). So, for instance, in acidic medium: (i) if the metal surface is negatively charged (according to potential of zero charge (PZC)), the cations (protonated molecules) would be “directly” adsorbed on the metal surface (Fig. 6a), (ii) if it is positively charged, it will be difficult for the protonated molecules to approach the metal surface because of the electrostatic repulsion. Thus, certain anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ...), present in solution, become firstly adsorbed on the metal surface creating an excess negative charge in the vicinity of the interface and favors more “indirect” adsorption of protonated molecules (Fig. 6b) [187,188]. In the second mode, the neutral molecules may be adsorbed on the surface of metal through “donor–acceptor” interactions (chemisorption mechanism) between: (i) the  $\pi$ -electrons of multiple bonds (doubles or triples) as well as the phenyl group with the vacant “d” orbitals of metal (Fig. 6c), (ii) unshared electron pairs of oxygen atoms of EOs molecules and vacant “d” orbital of metallic surface (Fig. 6c), (iii) the anti-bonding molecular orbitals (vacant  $p^*$ ) of the EOs molecules and the d-electrons of surface metal-atoms (reterodonation) in order to relieve the extra negative charge from the metal (Fig. 6d).



**Fig. 6** Simplified schema of mechanism of EOs in inhibition of metallic corrosion.



Generally, in the aqueous solution, the adsorption of EOs inhibitor molecules through mechanisms mentioned above can be considered as a quasi-substitution process between the inhibitor in the aqueous phase  $\text{Inh}_{(\text{sol})}$  and water molecules at the electrode surface  $\text{H}_2\text{O}_{(\text{ads})}$  [189] :



where x is the size ratio, that is, the number of water molecules replaced by one organic inhibitor.

## 6. Conclusion

This present work is the first extensive review describing the application of EOs as green corrosion inhibitor of various metals and alloys in different solutions, based on the research papers from the last 14 years (2004–2018). In total, 120 published papers described the anticorrosive activities of 72 different samples of EOs extracted from 76 plant species belonging to 18 distinct families. A thorough study of these researches revealed that almost tested EOs have been exhibited a good ability to use it as the green and sustainable inhibitors against corrosion of all studied metals because to their bio-degradability, eco-friendliness, low cost and easy availability and renewable sources of materials. WL and electrochemical (PDP and EIS) were the most frequently used techniques to evaluate the corrosion IE of the all studied green inhibitors. The protective layer (film) formed on the metal surface has been analyzed by FTIR spectroscopy, SEM coupled with EDX and XPS techniques. According to extracted results, generally all EOs acted as better corrosion inhibitors of the corrosion of all metals in a dose dependent manner. The IE increased significantly with increasing concentrations of the tested natural products in the different test media. This indicates that the active molecules of the extracts are adsorbed onto the metal surfaces, through the formation of insoluble intermediates, resulting in the blocking of the active sites and effectively isolating the metals and corrosive agents. Moreover, the IE of the majority of the studied materials decreased with increasing temperature in tested range. Based on the PDP measurements, the majority of the studies reported that these products were found to act as mixed-type inhibitors. Moreover, according to the thermodynamic calculations, the inhibition action of most of studied corrosion inhibitors occurs primarily through physisorption mechanism and follow Langmuir adsorption isotherm. In addition, the effectiveness of inhibiting corrosion by an EO is closely related to its chemical composition consisting generally of mixtures of phytochemical components including terpenic hydrocarbons and their oxygenated terpenoid

derivatives. Such complexity makes it rather difficult to accurately determine the exact contributions of the different components to the global inhibitory effect of the entire extract. Nevertheless, it is possible to the inhibition effectiveness of these extracts might be related to a specific molecules, especially major compounds, or those susceptible to be active, or to a synergistic effect of the entire extract. In this context, theoretical approaches using a computational study (DFT and MDS) is therefore necessary for future studies for studying interaction between individual constituents, especially major compounds isolated from EOs, and metal surface and their contributions to the inhibitory effect of the entire extract.

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